

## Surface pyroelectricity and surface piezoelectricity in organic and inorganic crystals

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While polarity is a property of only 10 out of 32 crystal classes, surfaces are inherently polar. Therefore, surface reconstruction in crystals may potentially lead to symmetry reduction producing pyroelectric and piezoelectric response generated from the near surface layer (NSL). Since both effects may incur significant surface charges, understanding the conditions at which surface acquire polarity is of particular practical and scientific interest.

The lecture will provide a review of the current understanding of surface polarity with the example of inorganic ( $\text{SrTiO}_3$ ) and organic crystals comprising of polar molecules (glycine, L-Asparagine, DL-alanine). Symmetry reduction in NSL may take place due to a number of reasons:

(a) Impurity-driven symmetry reduction is observed in glycine, L-Asparagine and some other crystals of amino acids. The impurity, most commonly incorporating into the crystals of amino acids, is the solvent used to grow the crystals. For the case of glycine, water incorporation was proven to be the cause of surface polar.

(b) Local disorder may be a source of polarity in racemic crystals, e.g., like DL-alanine, which exhibits strong pyroelectricity in non-polar crystallographic directions.

(c) Surface reconstruction in  $\text{SrTiO}_3$  forms a polar layer.

Thickness of NSL varies widely from a few angstroms of the case of  $\text{SrTiO}_3$  to a few tens of nm for the case of glycine. Detection and quantification of surface polarity poses considerable problem, especially if NSL has low pyroelectric coefficient and small thickness. The most efficient method for measuring surface pyroelectricity is a periodic temperature change (PTC, modified Chynoweth method). Mathematical modelling of the heat and electric current distribution shows that if the thickness of the polar layer,  $\delta$ , is much smaller than the thickness of the crystal,  $d$ , only the product  $\delta \cdot \alpha$ , where  $\alpha$  is the pyroelectric coefficient of the NSL, can be determined. In those cases, when  $\delta$  is known, e.g.  $\text{SrTiO}_3$ , or it is measurable, i.e.  $\delta/d \gg 0.05$ , the value of  $\alpha$  can be determined and, by integrating  $\alpha$  vs temperature, the absolute value of polarization can be deduced. For the case of water-induced NLS of glycine polarization is very weak (few  $\text{nC/cm}^2$  at best), while for the case of  $\text{SrTiO}_3$ , the polarization is comparable with that of  $\text{BaTiO}_3$  (few  $\mu\text{C/cm}^2$ ).

Detection of the piezoelectric effect of the NSL is more complicated because small values of  $\delta$  implies small absolute displacement. So far, the definite proof of surface piezoelectricity was provided only for glycine crystals because of the large value of  $\delta > 10 \mu\text{m}$ .

Thermodynamics of the polarization of NSL is not fully developed and the driving forces or polarization is not clear. However from the fact that polar NSL is far more frequently observed in molecular crystals rather than in inorganic crystals, suggest that the enthalpy of the crystal formation is a dominating factor. In this view, one can expect that surface polarity should be more probable in molecular crystals comprising polar molecules.